

Photoemission spectra and band structures of *d*-band metals. VI. Spin polarization of bulk photoemission from ferromagnetic Ni

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The photoelectron spin polarization from ferromagnetic Ni has been calculated using a combined interpolation scheme. The band structure was adjusted to reproduce the experimental magneton number and the correct E_F - L_2 separation as determined from recent angle-resolved photoemission experiments. Results of calculations are reported for emission from (100) and (111) surfaces and from polycrystalline samples. Major disagreement with experiment for the (100) surface indicates that surface photoemission is dominant near threshold. It is suggested that energy-resolved measurements will be required if bulk and surface emission are to be distinguished. Calculated energy spectra are reported and discussed.

I. INTRODUCTION

Since the early measurements by Banninger *et al.*¹ the photoelectron spin polarization (photo-ESP) of Ni and other ferromagnets has been of considerable interest. These early measurements were surprising in that they did not display the expected negative sign close to threshold. Interpretations were of two kinds. In the first kind,^{1,2} it was held that the results demonstrated a failure of the one-electron Stoner-Wohlfarth-Slater (SWS) band model of ferromagnetism. In the second kind,^{3,4} it was held that it was the photoemission process itself or the band structure which was imperfectly understood. As an example of the latter approach, Smith and Traum⁴ showed that when \vec{k} conservation was included in the calculations the predicted negative excursion of the spin polarization of the photoelectric yield occurred over a very narrow photon energy range close to threshold; they found also that only small changes in the band structure and work-function parameters were required to make the negative excursion disappear altogether. The calculations reported in this paper were undertaken in an attempt to refine the earlier calculations and to clarify just what features of the spin-polarized photoemission data can and cannot be accounted for using a simple band model.

It should be stated at the outset that our latest results are not notably successful in comparison with experiment—in fact, just the reverse. Shortly after the start of this project, new experimental results for the photo-ESP of Ni were published which displayed the expected negative sign at threshold.⁵ This did not remove the discrepancies with one-electron band theory as might be supposed. This was because the new measurements were performed on well characterized single-crystal surfaces. The earlier experiments

had been performed on evaporated (and presumably polycrystalline) samples. When the crystal surface is well defined an additional selection rule takes on special importance. This is the requirement that the parallel component \vec{k}_{\parallel} of the electron wave vector be conserved as the photoelectron crosses the sample surface. We have inserted this requirement into our new calculations and we show, as anticipated by Dempsey and Kleinman,⁶ that it leads to major disagreements with experiment. The inescapable conclusion is that *bulk* band theory, at least in the photon energy range a few eV above threshold, is quite incapable of explaining the photo-ESP and that the measurements are dominated by *surface*-derived photoemission processes.

II. CALCULATIONAL DETAILS

A. Parametrized band structure

The starting point of these calculations was an augmented-plane-wave (APW) calculation for paramagnetic Ni performed by Mattheiss.⁷ The combined interpolation scheme of Smith and Mattheiss⁸ was fitted to this band structure, and the parameters obtained are shown in Table I. The band structure for ferromagnetic Ni was then obtained by the empirical procedure described below. Two (and only two) basic pieces of experimental information were used: (a) the position of the $L_{2'}$ level as determined by angle-resolved photoemission⁹; and (b) the known magneton number of 0.56 Bohr magnetons per atom. These experimental constraints remove much of the arbitrariness of the band structure which had plagued our earlier calculations.

Recent angle-resolved photoemission measurements on Ni(111) have placed the $L_{2'}$ level 0.75 eV below the upper $L_{3\uparrow}$ level of the majority-spin

TABLE I. Parameters of the combined interpolation scheme for Ni: (a) fit to paramagnetic APW results of Mattheiss; (b) majority- and (c) minority-band structures of ferromagnetic Ni after empirical adjustments.

	(a) Fit to APW	(b) Majority spin	(c) Minority spin
<i>d</i> bands			
E_0	0.5459	0.5724	0.6010
Δ	0.0028	0.0029	0.0030
A_1	0.02684	0.02764	0.02851
A_2	0.00771	0.00794	0.00819
A_3	0.01028	0.01058	0.01092
A_4	0.01498	0.01542	0.01591
A_5	0.00347	0.00357	0.00369
A_6	0.01225	0.01261	0.01301
plane waves			
α	0.01487	0.01487	0.01487
V_{000}	-0.0115	-0.0115	-0.0115
V_{111}	0.0879	0.0879	0.0879
V_{200}	0.1095	0.1095	0.1095
hybridization and orthogonalization			
B_t	1.308	1.327	1.348
B_e	1.296	1.315	1.336
S	0.910	0.910	0.910
R^a	0.410	0.410	0.410

^aNot treated as disposable.

d band.⁹ We shall be assuming, in concordance with first-principles spin-polarized band calculations,^{10,11} that the energies of the L_2 level and other predominantly *s, p*-like levels are essentially the same in the majority- and minority-spin band structures. An L_3 - L_2 separation of 0.75 eV is readily obtained by raising the *d* bands in Mattheiss' APW calculation by 0.0265 Ry relative to the *s, p* bands. (See below for further details of the actual parameter adjustments.) This will then serve as the majority-spin band structure. A precise density of states was then calculated using this band structure, and E_F was set at that energy which just encloses 5.28 electrons per atom. The separation of E_F and the uppermost majority *d* band are then given by $E_F - L_3^{\uparrow} = 0.32$ eV and $E_F - X_5^{\uparrow} = 0.13$ eV. The former is in reasonable agreement with the angle-resolved photoemission results of Ref. 9. The smallness of these values is consistent with the estimates of Wohlfarth.^{3,12} To obtain the minority-spin band the *d* band was again raised until the number of electrons remaining below the previously determined E_F was 4.72 per atom.

When the *d* band was raised in the adjustments described above, its width was simultaneously increased. This is in accordance with the re-

sonance approach.¹³ The following recipe simulates the actual relation between *d*-band position and *d*-band width found by Connolly.¹¹ We use the same nomenclature as in Ref. 8. For a shift ϵ in E_0 , 0.03ϵ was added to A_1 ; all other A_n 's and Δ were scaled as A_1 , and the hybridization parameters B_t and B_e were scaled as $A_1^{1/2}$. The final parameters obtained for the ferromagnetic Ni are shown in Table I, and the bands are illustrated in Fig. 1. Since we have simulated the ferromagnetic band structure by adjusting only the *d* bands, the minority bands (dashed curves) almost exactly coincide with the majority bands (full curves) over the whole *s, p* range.

The mean exchange splitting is 0.029 Ry (0.40 eV). Because of the variation of *d*-band width as a function of position discussed above, the exchange splitting at the top of the *d* band is slightly larger than the mean value and the value at bottom of the *d* band is slightly smaller. This is consistent with the results of first-principles band calculations.^{10,11} The value of the mean exchange splitting is lower than those obtained in first-principles calculations. There is a direct linkage between the exchange splitting and the position of the *d* bands relative to the *s, p* bands. The new angle-resolved photoemission results place the *s, p*-like L_2 level lower with respect to *d* bands than in previous work. This has the effect of drawing *s, p* electrons below the top of the *d* bands. This means that it is necessary to go only a small distance above the top of the *d* bands in the majority-spin band structure to enclose 5.28 electrons per atom.

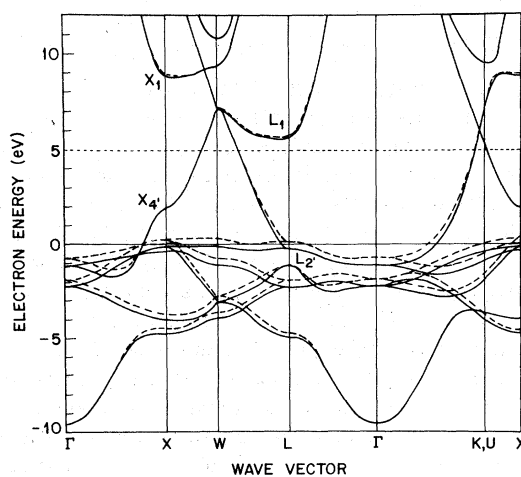


FIG. 1. Combined-interpolation-scheme band structure for ferromagnetic Ni. Full (dashed) curves represent the majority- (minority-) spin bands. Energies (in eV) are measured from the Fermi level.

B. Photoemission and band structure

The calculations of the photo-ESP were performed by the following approximate method. The energy distribution of photoemitted electrons is related to the bulk band structure by the well known Brillouin-zone integrals:

$$N(E, \hbar\omega) \propto \sum_{f,i} \int_{\text{BZ}} d^3k |P_{fi}|^2 D(E_f, \vec{k}) T(E_f, \vec{k}) \times \delta(E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega) \delta(E - E_i(\vec{k})). \quad (1)$$

This expression is based on the three-step model and assumes that \vec{k} is conserved in the optical transition. In this work the square of the momentum matrix element $|P_{fi}|^2$ and the transport factor $D(E_f, \vec{k})$ will be kept constant. The escape factor $T(E_f, \vec{k})$ was not kept constant, and its form was adjusted to simulate emission from single-crystal surfaces or from polycrystalline samples.

In the case of emission from single-crystal surfaces we put

$$T(E_f, \vec{k}) = \begin{cases} 1, & \text{if } E_f - E_v > \hbar^2 k_{\parallel}^2 / 2m, \\ 0 & \text{otherwise,} \end{cases} \quad (2)$$

where E_v is the vacuum level and \vec{k}_{\parallel} is the component of \vec{k} parallel to the surface. This relation merely expresses the requirement of conservation of k_{\parallel} at the surface. Two specific crystal faces were considered, (100) and (111). A third set of calculations were performed in which k_{\parallel} conservation at the surface was not applied. In this case we put

$$T(E_f, \vec{k}) = \frac{1}{2} [1 - (E_v - E_B)^{1/2} / (E_f - E_B)^{1/2}], \quad (3)$$

where E_B is the energy of the bottom of the effective free-electron potential well. ($E_v - E_B$ will be recognized as the inner potential.) Equation (3) is the semiclassical escape function and is independent of \vec{k} . Physically this might correspond to emission from a polycrystalline sample whose surface consists of many different crystal faces. The calculations performed using Eq. (3) for $T(E_f, \vec{k})$ will therefore be referred to as the "polycrystalline" calculations. The Brillouin-zone integral was performed numerically in the manner described in previous papers.^{14,15}

Calculations were performed separately for $N_{\uparrow}(E, \hbar\omega)$ and $N_{\downarrow}(E, \hbar\omega)$, the photoelectron energy spectra for the majority- and minority-spin band structures, respectively. The corresponding photocurrents $J_{\uparrow}(\hbar\omega)$ and $J_{\downarrow}(\hbar\omega)$ are obtained from

$$J_{\uparrow}(\hbar\omega) = \int_{E_v - \hbar\omega}^{E_F} N_{\uparrow}(E, \hbar\omega) dE, \quad (4)$$

and the photo-ESP is defined as

$$P = (J_{\uparrow} - J_{\downarrow}) / (J_{\uparrow} + J_{\downarrow}). \quad (5)$$

P rather than $N_{\uparrow}(E, \hbar\omega)$ is the quantity presently measured experimentally.

III. RESULTS AND DISCUSSION

A. Photoelectric yield

To make contact with the earlier work of Ref. 4, we present first the results for the polycrystalline calculations of the photo-ESP. These are shown in Fig. 2 for several values of the work function Φ ($\equiv E_v - E_F$). The values $\Phi = 6$ and 7 eV are unphysically high. The values $\Phi \lesssim 5$ eV can be achieved by the process of cesiation. It is noted that in each case the photo-ESP is negative at threshold and then changes sign at slightly higher values of $\hbar\omega$.

The width of the negative excursion is seen to be a function of Φ , being narrowest in the region $\Phi \sim 5$ eV. This effect can be traced to a feature common to all the fcc d -band metals, namely the existence of a region in the $E - \hbar\omega$ plane in which the energy distribution of the joint density of states (EDJDOS) vanishes (i.e., a region for which no \vec{k} -conserving transitions are possible). In the cases of Rh and Ir, which have one less valence electron per atom than Ni, this region is intersected by the Fermi level. This effect, which should be observable as a movement of the leading edge of the

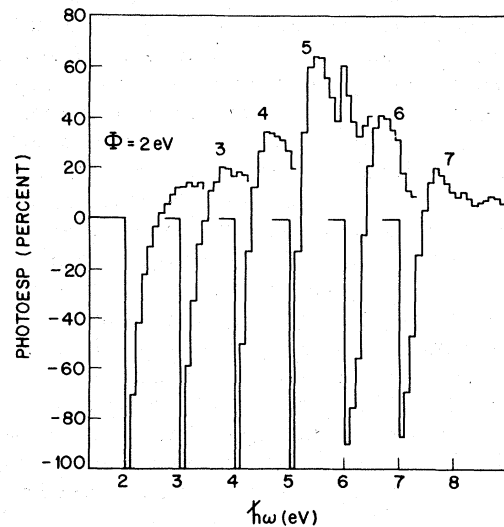


FIG. 2. Photoelectron spin polarization calculated for a "polycrystalline" sample at various values of the work function Φ .

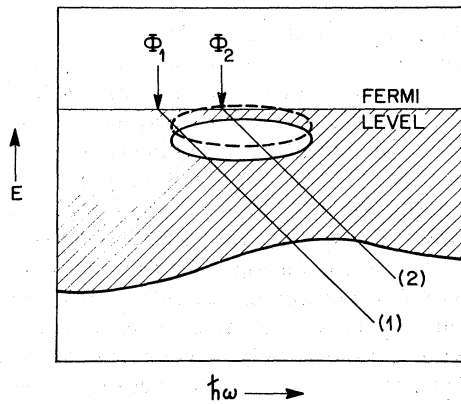


FIG. 3. Schematic representation of the ENJDOS for the *minority*-spin band structure. The cross hatched region corresponds to the occupied states for which the EDJDOS is nonzero. Of these the states which can give rise to photoelectrons are those lying above the vacuum level represent by the line (1) or (2). The majority-spin ENJDOS would look similar but shifted downwards in energy.

spectra to lower initial energies, has been remarked upon in earlier papers of this series.^{14, 16} In the case of Ni, the region of zero EDJDOS for the *minority*-spin bands lies *just* below the Fermi level. This is illustrated schematically in Fig. 3. It is seen that the width of the region between E_F and the upper edge of the zero-EDJDOS region varies with $\hbar\omega$. This is what accounts for the variation with Φ of the negative excursion of the photo-ESP at threshold.

For certain parametrizations of the Ni band structure the Fermi level just intersects the region of zero-EDJDOS for the *minority* spins. This is true, for example, for Hodges' "b" parameters¹⁷ used in the calculations of Ref. 4. The situation is represented by the dashed curve in Fig. 3. The photo-ESP at threshold can be either positive or negative depending on the value of Φ . If $\Phi = \Phi_1$ (shown in Fig. 3), the photo-ESP will be negative at threshold. (The *minority* electron states which contribute to the photo-ESP are those which fall in that part of the cross hatched area lying above and to the right of the 45° line labeled 1.) If $\Phi = \Phi_2$, on the other hand, the threshold occurs in the region of zero-EDJDOS for the *minority* spins; since the *majority*-spin EDJDOS is always nonzero close to E_F the photo-ESP is positive by default. This feature of the Hodges "b" parametrization is the origin of the statement in Ref. 4 that "the existence of this feature (the negative excursion and the dramatic reversal of sign just above threshold) is rather sensitive to the choice of Φ , E_F , and the specific band model." In our more recent

parametrizations, including the one used in this paper, the Fermi level does not intersect the zero-EDJDOS region.

The polycrystalline case is rather artificial and has been rendered obsolete by the new measurements⁵ on single-crystal surfaces. The main purpose of the preceding discussion is to clarify some imperfectly understood points concerning the predictions of the one-electron SWS band model of ferromagnetism. It has emerged that alternative (and seemingly equally plausible) band structures of Ni predict *either* a positive *or* negative photo-ESP at threshold. Contrary to earlier assertions, the observed sign of the threshold photo-ESP in polycrystalline samples is therefore equivocal as far as the validity of the SWS model is concerned. Let us turn now to the results for single-crystal surfaces. These are likewise indecisive on the validity of the SWS model, but shed a lot of light on the importance of surface as opposed to bulk effects.

The results of the calculations of the photo-ESP for emission from the (111) and (100) surfaces of Ni are shown in Fig. 4, where they are compared with the calculated results for the polycrystalline case. For convenience Φ was set

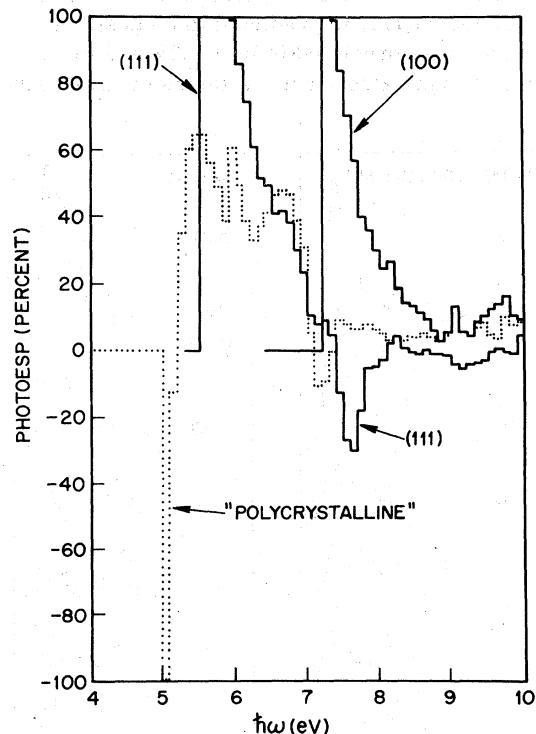


FIG. 4. Calculated photoelectron spin polarization for emission from a polycrystalline surface and from the single-crystal surfaces (111) and (100) of Ni.

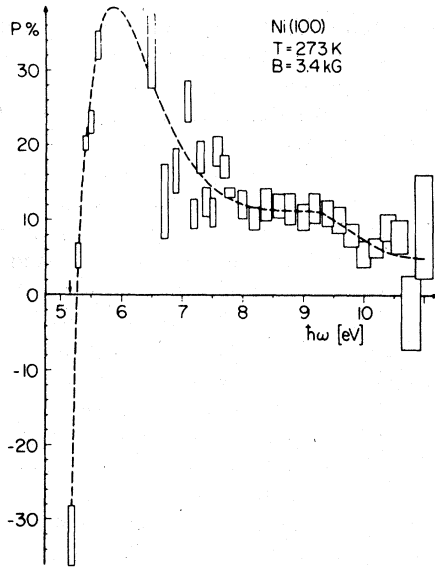


FIG. 5. Photoelectron spin polarization for emission from Ni(100) measured experimentally by Eib and Alvarado (Ref. 5).

equal to 5.0 eV in each case. The actual experimental values for Φ vary slightly from face to face, but this will not affect our main conclusions. It is seen that at onset the photo-ESP from both Ni(100) and Ni(111) is predicted to be positive; moreover it is predicted to be +100% and to remain at a high value for a few tenths of an eV above

onset. Note that the *onset* at $\hbar\omega = 5.5$ and 7.2 eV for Ni(111) and Ni(100), respectively, occurs at photon energies above the *threshold* of $\hbar\omega = 5.0$ eV. This is a consequence of the large band gaps at L and X . At threshold the emerging photoelectrons have essentially zero kinetic energy, so that we must have $k_{\parallel} = 0$. This means that at threshold we sample only electrons along the ΓL or ΓX directions for Ni(111) or Ni(100), respectively. It is seen from Fig. 1 that the minimum energies for photoelectron states correspond to the $L_{1\uparrow}$ and $X_{1\uparrow}$ levels which occur at 5.6 and 8.9 eV above E_F , respectively. These are both above the vacuum level (5.0 eV) in our present model. The onsets in Fig. 4 occur at photon energies slightly lower than the $L_1 - E_F$ and $X_1 - E_F$ separations. This is because Eq. (4) can be satisfied for certain states with $k_{\parallel} \neq 0$ at energies lower than L_1 and X_1 but above threshold.

The experimental results of Eib and Alvarado⁵ for the photo-ESP from Ni(100) are shown in Fig. 5. It is seen that they are in gross disagreement with the bulk band structure prediction of Fig. 4. The bulk contribution predicted to occur abruptly at $\hbar\omega = 7.2$ eV may be associated with one of the apparent structures in this energy range in the measured photo-ESP; the statistical uncertainty of the data, however, is too large to make any definitive statement. In any case, the predicted bulk contribution, if present, would appear to be severely diluted by other processes, presumably of a surface origin. Such observations are now

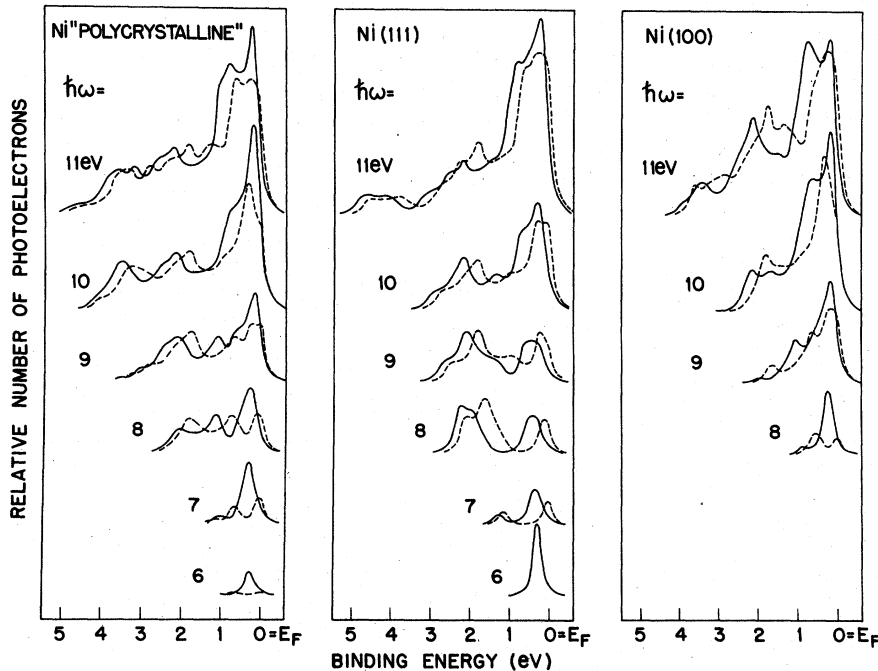


FIG. 6. Spin-polarized photoelectron energy spectra (angle-integrated) calculated from the bulk band structure. Full (dashed) curves correspond to majority (minority) spin electrons.

fairly commonplace. For example, Feuerbacher and Christensen¹⁸ discovered normal photoemission from various crystal faces of W which occurs in an energy range corresponding to absolute gaps in the band structure. Likewise, Rowe and Smith¹⁵ observed d -band emission from Cu(100) which was forbidden in the bulk band-structure model. These effects are now referred to as "band-gap emission" and are thought to involve optical transitions to final states which are propagating waves outside the crystal but evanescent on the inside. The nature of the initial state is not usually specified. Dempsey and Kleinmann⁶ propose that the photo-ESP of Ni(100) is explicable in terms of emission from an initial surface state. This is a strong possibility, but we cannot exclude the possibility that only surfacelike final states are involved.

B. Energy spectra

The photo-ESP, being a highly integrated quantity, is a rather blunt tool with which to reveal bulk band-structure effects. Energy-resolved data would be preferable. Experimentally this represents a rather formidable proposition, and work of this nature is only just beginning.¹⁹ In anticipation that such experiments will eventually be performed, we show in Fig. 6 the spin-polarized angle-integrated photoelectron energy spectra calculated from Eq. (1). The three cases Ni(100), Ni(111), and polycrystalline Ni are shown, and in each case we have taken $\Phi = 5.0$ eV. The results illuminate perhaps more clearly how the photo-ESP evolves close to onset. Well away from onset the spectra look quite similar for the three cases. Presumably as the escape cone defined by either Eq. (2) or (3) opens up we quickly reach a situation where we are sampling most of

the Brillouin-zone (or the irreducible $\frac{1}{48}$ th of it) regardless of the experimental conditions. This should prove of value in future attempts to separate bulk from surface contributions in experimental photoemission spectra.

IV. CONCLUDING REMARKS

Calculations have been reported for the bulk band-structure predictions of the photo-ESP from Ni. The results, particularly those for Ni(100), do not account for the experimental observations, and we must conclude that the photo-ESP within a couple of eV of threshold is dominated by surface-derived photoemission. This supports the second kind of viewpoint described in the Introduction. Our understanding of the photoemission process is too imperfect to derive any information on the validity of SWS theory from the photo-ESP. Such information does appear to be obtainable from angle-resolved photoemission.⁹

The calculations presented here are rather crude and could be improved, for example, by inclusion of the factors $|P_{fi}|^2$, $D(E_f, \vec{k})$ in Eq. (1). The succeeding paper in this series will describe a simple and straightforward way of evaluating $|P_{fi}|^2$. The width of the d band could also be adjusted to be in closer agreement with experiment.⁹ In view of the proven dominance of surface effects in the photo-ESP near threshold, such refinements do not seem to be worthwhile at present, but will be of value when energy-resolved measurements have been performed.

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